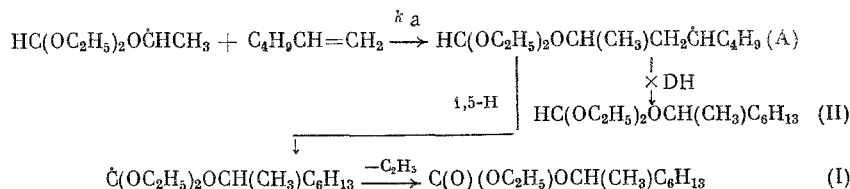


TABLE 2. Addition of Orthoformate Ester (S) to 1-Hexene (M). Initiator, tert-Butyl Peroxide (140°C, 1 h)

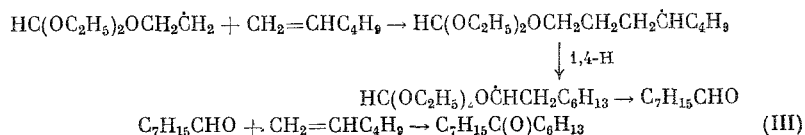
Amounts, mmoles		Conversion, %		$\left(\frac{M}{S}\right)_{av}$	[M] _{av}	Distribution of reaction products, mole %		$\frac{k_{CH}}{k_{CH_2}}$	$\frac{k_f}{k_a}$, mole/liter			
M	S	M	S			HC(O)OC ₂ H ₅	(C ₂ H ₅ O) ₂ CO			adduct (I)	ketone (III)	
0,5	10	25,2	14,4	0,05	0,12	35,9	57,7	5,8	0,6	1,4	0,76	
0,6	10	22	14,2	0,06	0,14	31	62,0	7,0	-	1,7	0,63	
1	10	20,8	15,5	0,1	0,24	31,9	57,9	9,6	0,6	1,4	0,83	
2	10	19,4	15,4	0,2	0,47	23,3	59,5	15,5	1,7	1,5	0,71	
3	10	7,1	5,6	0,3	0,77	20,5	53,8	20,6	5,1	1,3	0,77	
4	10	12,8	10,5	0,4	1,04	15,5	52,1	26,8	5,6	1,5	0,60	
5	10	8,2	10,3	0,5	1,19	18,7	54,7	20,3	6,3	1,4	1,1	
									Mean		1,5±0,1	0,77±0,1

$$* \frac{k_{CH}}{k_{CH_2}} = \frac{[(C_2H_5O)_2CO]}{[HC(O)OC_2H_5] + [I]} \cdot \frac{k_f}{k_a} \frac{[M] [HC(O)OC_2H_5]}{[I]} \quad (II)$$

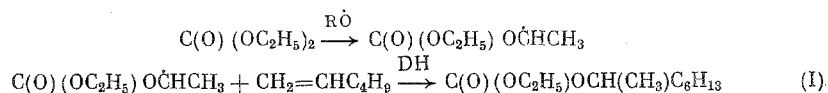
formation of adduct (I) is accounted for by a route involving rearrangement of the radical-adduct A, with 1,5-migration of hydrogen and fragmentation of the isomerized radical-adduct with elimination of the ethyl radical



No orthoester of heptanoic acid was found in the reaction mixture, indicating that the fragmentation of the $\dot{\text{C}}(\text{OC}_2\text{H}_5)_2$ radical was much more rapid than its addition to 1-hexene. We have previously observed similar behavior in a study of the radical telomerization of ethylene with straight-chain acetals [3], in which it was found that the $\dot{\text{C}}\text{H}(\text{OCH}_3)_2$ radical did not react with ethylene to give the acetals of higher aldehydes, but fragmented completely to give methyl formate. The rapid rearrangement of the radical-adduct A with 1,5-hydrogen transfer, as shown by the absence of the orthoester (II) from the reaction products, perhaps results from the ease of homolysis of the $\text{H}-\text{C}(\text{OC}_2\text{H}_5)_2$ bond and also from the nature of the six-membered transition state which incorporates an oxygen atom. The formation of the ketone (III) with two unbranched hydrocarbon chains of differing lengths (^{13}C NMR data) suggests that the reaction proceeds in part at a C-H bond of the methyl group



The proportion of the ketone (III) was no more than 1-6% of the total reaction products (Table 2), i.e., this reaction pathway is not of great importance. Experiments carried out under strictly controlled conditions over the range of ratios of 1-hexene to orthoester 0.05-0.5 enabled the ratio of the rate constants for the removal of hydrogen from C-H groups (k_{CH}) and CH_2O (k_{CH_2}) to be compared. This ratio describes the relative reactivities of these groups (Table 2). The value found for this ratio (1.5) is close to the ratio of these constants found in a study of the fragmentation of the orthoester in the presence of tert-butyl peroxide [2]. In the orthoformate ester molecule, there are six C-H bonds in CH_2O groups per formyl C-H bond. Bearing in mind this statistical factor, the formyl C-H bond is an order of magnitude more reactive than the C-H bond in the alkoxy group. In these experiments, we also determined the rate constant for the fragmentation (k_f) and addition (k_a) of the $\text{HC(OC}_2\text{H}_5)_2\text{O}\dot{\text{C}}\text{HCH}_3$ radical to 1-hexene. It was found to be close to unity (0.8 mole/liter). The amounts of diethyl carbonate formed in the experiments were sensibly constant, and were not dependent on the hexene-orthoester ratio or the yield of adduct (I) (Table 2), showing that the yield of diethyl carbonate is determined by the ratio $k_{\text{CH}}/k_{\text{CH}_2}$. However, as the proportion of the adduct (I) increased, the proportion of ethyl formate decreased, although the sum of their yields remained approximately constant. These findings provide support for the formation of adduct (I) by the route described above: During its formation, as a result of secondary reactions of the diethyl carbonate present in the reaction mixture with 1-hexene, any increase in the yield of the adduct should result in a substantial reduction in the proportion of ethyl carbonate:



The structure of adduct (I) was confirmed by the presence in its ^{13}C NMR spectrum (Table 1) of signals typical of the functional group $^{13}\text{C}(\text{O})(\text{OR})_2$, and the ^{13}CHO and $^{13}\text{CH}_3\text{CH}$ groups, confirming the addition of 1-hexene at the orthoester CH_2O , and the presence of a signal for the $\text{CH}_3-^{13}\text{CH}_2\text{O}$ group shows that the carbonate molecule retains one of the two ethoxy groups. The chemical shifts of the remaining signals, and the ratios of their intensities, are in accordance with the assignments made. The ketone (III) showed signals characteristic of the ^{13}CO and $^{13}\text{CH}_2\text{C(O)}-^{13}\text{CH}_2$ groups, the latter being twice as intense.

EXPERIMENTAL

^{13}C NMR spectra were obtained on a Bruker-Physik HX-90 spectrometer, operating frequency 22.635 Hz, internal standard CCl_4 , chemical shifts measured relative to TMS.

Preparative GLC was carried out on a PAKhV-01 apparatus, column 1200×9 mm with 15% SKTFT-50 on Chromatone N-AW, and GLC analyses were carried out on an LKhM-8MD-5, column 3000×3 mm with 5% SKTFT on Chromatone N-AW, catharometer, helium.

Addition of Ethyl Orthoformate to 1-Hexene. Preparative experiments were carried out in sealed glass ampuls (30 ml) under nitrogen, with 18 g of the orthoester, 10 g of 1-hexene, and 2 g of tert-butyl peroxide. The reaction mixture was heated in an oil bath at 140°C for 2 h, the ampuls being rotated in metallic sleeves. Eight similar experiments were carried out, and the products combined. Following removal of the starting materials by distillation, there was obtained 18.1 g of mixed products. This mixture was fractionated to obtain narrow fractions of adduct (I) and ketone (III) (weights of fractions, 4.9 g), and the narrow fractions were further purified by preparative GLC.

The kinetic experiments were carried out similarly, in 3-ml ampuls. The experimental conditions and GLC analyses are shown in Table 2.

CONCLUSIONS

1. The homolytic addition of ethyl orthoformate to 1-hexene is accompanied by fragmentation and isomerization of the intermediate radicals, as a result of which the adduct ethyl 2-octyl carbonate is formed.

2. The formyl C-H bond in ethyl orthoformate is approximately an order of magnitude more reactive than the α -C-H bond of the ethoxy group.

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